# I. ELECTROMETRIC TITRATION STUDIES

## A. DETERMINATION OF THE SAPONIFICATION NUMBER

## B. DETERMINATION OF THE HARDNESS IN WATER BY THE PALMITATE METHOD

# II. DEXTROSE-LEVULOSE INTERCONVERSION

BY

JAMES EARL REINSCHREIBER

B.S., University of Illinois, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

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R. UNIV. BIBLIOTHEEK LEIDEN

# I. ELECTROMETRIC TITRATION STUDIES

## A. DETERMINATION OF THE SAPONIFICATION NUMBER

### Introduction

One of the more common methods of analysis for fats and oils is the determination of the saponification number. The official procedures prescribed by the American Oil Chemists' Society (1) and the Association of Official Agricultural Chemists (2) are only slight modifications of the original method proposed by Koettstorfer (3) in 1879. This indicates a reasonable degree of satisfaction with and reliability for the method. Experience with a group of students in a course in food analysis, has shown that the values reported for the same sample have varied considerably, even when the reagents were taken from the same stock solutions, and it is possible that in many cases a good agreement in values obtained may be the result of close duplication of conditions for each analysis and may not represent real theoretical values.

It was the intent of this investigation to determine whether these variations could be attributed to random human error or to some variables in the determination procedure.

### Experimental And Results

A series of titrations on synthetic samples of soap and potassium hydroxide in an ethanol and water solvent mixture were followed potentiometrically with a Beckman pH meter. The nature of these curves and the pH at which the phenolphthalein end point is observed show that in the determination of the saponification number, successful titrations may be made in solutions of the soap, in which the ethanol content is 35 percent or more.

As a test of the procedure in actual practise, a series of

determinations of the saponification value of olive oil was made by the official method (1). The resulting data were submitted to a statistical analysis which verified the previous findings, that no significant variation in the calculated saponification number occurs if the ethanol content is greater than 34 percent.

Studies were made on the effect of exposure of samples to air. An analysis of variance of the data indicated that the effect of absorption of carbon dioxide is negligible, even up to a five hour exposure of the solutions to the atmosphere, and that it makes no difference whether blanks are exposed the same as the samples or if they are immediately titrated.

It is indicated that the variations observed in the results of a group of students who carried out the saponification determination were caused by human operational error and not by any inherent factors in the determination procedure.

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## B. DETERMINATION OF THE HARDNESS IN WATER BY THE PALMITATE METHOD

### Introduction

In 1937, Suter, (2) modified the original Blacher palmitate method (1) for the determination of hardness in water. Briefly, the method consists in the titration of the sample with a solution of potassium palmitate in a solvent mixture containing 42 percent glycerol and 58 percent U.S.P. ethyl alcohol. Although Suter's procedure increased the precision

over that of the earlier methods, the slow transition in color of the phenolphthalein indicator end point contributed an element of uncertainty to the determination. It was believed that this might be overcome by following the reaction electrometrically with a pH meter.

### Experimental And Results

Investigations were made of factors that enter into the reaction of alkaline earth ions with palmitate ions by following the reactions under carefully controlled conditions with a Beckman pH meter. The more important factors investigated were apparent pH and solvent composition of the potassium palmitate reagent, pH of the hardness containing sample before titration with the potassium palmitate reagent, and substitution of potassium hydroxide for sodium hydroxide in the adjustment of the pH of the hardness containing sample.

As a result of the investigations, a modified procedure was developed which doubled the precision of the Suter method (the standard procedure for the American Water Works Association).

Eleven alkaline earth compounds were investigated as possible primary standards for hardness. Iceland Spar calcite crystals and spectroscopically pure magnesium metal were found to be most suitable.

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## II. DEXTROSE-LEVULOSE INTERCONVERSION

### Introduction

Levulose, which is sweeter and more soluble than dextrose,

is not available in a pure state at a price comparable to dextrose or sucrose. A possible inexpensive method of manufacture would be the conversion of dextrose to levulose, followed by separation of the levulose from the conversion mixture.

Lobry de Bruyn (5) first recognized the equilibria that exist between various hexoses under alkaline conditions. Since then, many investigators have studied the interconversion equilibria of hexoses, particularly of dextrose and levulose. Results have varied although equilibrium conditions studied were similar. These variations seem to be caused by the investigators' choice of method of analysis.

This investigation was concerned with the conversion of dextrose to levulose in phosphate buffer solutions at various pH levels, ranging in value from 4.5 to 12.0. Involved in this study was the determination of the effect and importance of cyclic-acyclic equilibria of dextrose and of levulose on the more common chemical methods of analysis as well as on optical rotation measurements.

## Experimental And Results

Investigations were made on the conversion of dextrose to levulose at 121° C (autoclaving conditions) in phosphate buffers in the pH range 6.0 to 7.0 by the Englis-Hanahan method (2) and on the interconversion of dextrose and levulose at room temperature in phosphate buffers, pH 4.5 to 12.0.

*Conversions at 121° C.* The combined results from the following methods of analysis; Lane-Eynon total reducing sugar (4), Becker-Englis selective ketose (1), double temperature polarization for levulose (3), total fermentation, ultraviolet absorption, and partition chromatography (6) indicated these conversions to levulose in the autoclaved samples; 18.40-19.40 percent at initial pH 6.00, 22.60-24.60 percent at initial pH 6.50, and 26.00-30.70 percent at initial pH 7.00.

Acyclic forms of dextrose and levulose as well as small

amounts of degradation products were indicated to be present and to be the cause of discrepancies between the chemical selective ketose methods and the double temperature polarization methods of analysis for levulose.

*Interconversion studies at room temperature.* Interconversion between dextrose and levulose in phosphate buffers at room temperature approaches an equilibrium as the pH is increased. With levulose, the equilibrium is approached at a faster rate than with dextrose.

The single temperature polarization method of analysis was shown to be highly unsatisfactory for sugar solutions of high pH.

Levulose formed compounds with phosphate at high pH to such an extent that partition chromatography also was unsatisfactory as a method of analysis.

The differences in the results of double temperature polarization and of chemical (iodimetric aldose and Becker-Englis selective ketose) methods of analysis became more pronounced in the higher pH solutions. Ultra-violet absorption studies confirmed the presence of acyclic forms of the sugars and partition chromatography studies indicated that increasing amounts of degradation products, as well as the acyclic form of dextrose, were produced as the pH was increased.

Dextrose at an initial pH 12.0 gave the maximum conversion to levulose. After 90 hours at room temperature, at least 25 percent levulose was formed (cyclic form indicated by double temperature polarization analyses) as compared with the maximum value of 38 percent (chemical methods of analysis).

*Comparison of the two conversion conditions.* The better method of conversion is autoclaving dextrose solutions in phosphate buffers at comparatively low pH, rather than using high pH at lower temperatures. About the same percentage conversion is obtained by the two methods but autoclaving is

a more rapid process and less degradation takes place.

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## VITA

James Earl Reinschreiber was born March 24, 1923, in Chicago, Illinois, and received his primary and secondary education in the public schools there. He entered the University of Illinois in 1941 and received his B. S. degree in chemistry in 1944, as a member of the Navy V-12 unit.

After service in the South Pacific Area, he was honorably released to inactive duty in 1946, when he returned to the University of Illinois to enter the graduate school.

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He has published the following paper:

"Determination of Saponification Number", Anal. Chem., 21, 602 (1949). (With D. T. Englis.)